BOLTZMANN'S DISTRIBUTION LAW

SERIES IN PHYSICS

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Monographs·

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BOLTZMANN'S DISTRIBUTION LAW

by

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PREFACE

"Par ma foi, il y a plus de quarante ans
que je dis de la prose, sans que j'en
susse rien, et je vous suis le plus obligé
du monde de m'avoir appris cela."

MOLIÈRE
"*Le Bourgeois Gentilhomme*"

This booklet describes a course for students of physics and chemistry in their first term at a university provided they have passed G.C.E. at advanced level in pure mathematics, applied mathematics, physics and chemistry.

The idea of such a booklet was conceived at a discussion meeting arranged by the Low-Temperature Group of the Physical Society and described in Nature vol. 159, page 626. For eight years I have hoped that it might be written by someone more experienced than 1 am in elementary teaching, but I have now lost hope. If some students, after digesting the text of this booklet, later on react to a formal course of statistical thermodynamics somewhat as the Bourgeois Gentilhomme reacted to his lesson on prose I shall have succeeded in my object.

I am grateful to the publishers for doing everything possible to keep down the price and I for my part have aimed at the maximum brevity consistent with what I hope is an acceptable degree of clarity.

E. A. G.
1955

PREFACE TO SECOND PRINTING

Advantage has been taken of the reprinting to correct a mistake on page 7. There is no other change.

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E. A. G.

1958

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Chapter

ELEMENTS OF QUANTUM THEORY

Our present detailed knowledge of the structure of atoms and molecules has been acquired entirely since the turn of the century. Its acquisition has been due to a combination of new experimental techniques with a new theory of mechanics called "quantum theory". Some knowledge of quantum theory is essential for any detailed description of the behaviour of atoms and molecules. This chapter is devoted to a summary of the minimum amount of quantum theory adequate for our purpose. No mention will be made of the history of the development of quantum theory nor of the experiments which led to its development. The justification of the theory is, of course, that it leads to conclusions in agreement with experiment.

As an introduction to quantum theory, we shall recapitulate some of the elements of classical mechanics. We shall then describe the most essential modifications introduced by quantum theory. Classical mechanics is based on Newton's laws of motion. One of the consequences of these laws is the existence of energy which may be of two kinds, kinetic and potential. In an isolated system, e.g. a swinging pendulum, the total energy remains constant. As the potential energy decreases, the kinetic energy increases and vice-versa so that the sum of the kinetic energy and potential energy remains constant. For example the motion of a harmonic oscillator is completely described by the following equations, in which x denotes the positional coordinate, a the amplitude, ν the frequency and t the

time. Further, T denotes the kinetic energy, V the potential energy and E the total energy. The potential energy V has its minimum value, conventionally taken as $V = 0$, at $x = 0$.

$$x = a \sin 2\pi\nu t$$

$$\dot{x} = 2\pi\nu a \cos 2\pi\nu t$$

$$T = \tfrac{1}{2}m\dot{x}^2 = \tfrac{1}{2}m (2\pi\nu a)^2 \cos^2 2\pi\nu t$$

$$V = \tfrac{1}{2}m (2\pi\nu)^2 x^2 = \tfrac{1}{2}m (2\pi\nu a)^2 \sin^2 2\pi\nu t$$

$$E = T + V = \tfrac{1}{2}m (2\pi\nu a)^2$$

Thus the total energy E is proportional to the square of the amplitude a.

Whereas the total energy of an isolated mechanical system such as a harmonic oscillator remains constant, its energy can be changed by interaction with its surroundings. When the system gains energy, then the same amount of energy is lost by the surroundings and we say that work is done on the system by the surroundings. Conversely when the system loses energy then the same amount of energy is gained by the surroundings and we say that work is done by the system on the surroundings.

It is an essential feature of classical mechanics that the possible values of E form a continuum and that E changes continuously. It is an essential feature of quantum theory that E can have only certain discrete values and that E can change only from one of these discrete values to another. It is evident from this that there is in principle a complete contradiction between classical mechanics and quantum theory, but in fact the gaps between successive values of E are so small as to be entirely negligible for planets, projectiles and even the smallest grains of dust. They are however not always negligible for molecules and atoms and they are never negligible for electrons. Hence classical mechanics is an approximation to quantum theory valid for planets, projectiles and grains of dust but

sometimes inadequate for molecules and atoms and completely misleading for electrons.

The restriction of the energy E to discrete values is called "quantization". Quantum theory is largely concerned with the derivation from a few general principles of the rules of quantization. We shall not here be concerned with these derivations, but shall confine ourselves to quoting the derived rules for a few of the simplest and most important kinds of system.

The quantization rules involve a universal constant called "Planck's constant". This constant, denoted by h, has the dimensions of the product of linear momentum by distance i.e. the same dimensions as angular momentum. The value of h is 6.625×10^{-27} g cm^2 s^{-1} or 6.625×10^{-34} kg m^2 s^{-1}. We shall now quote and discuss several quantization rules in turn.

(a) As our first and simplest example we consider a particle of mass m moving freely back and forth between and normal to two parallel walls distant L apart. The quantization rule is expressed most simply in terms of the momentum $p \equiv m\dot{x}$, where x denotes distance from one of the walls and $\dot{x} \equiv dx/dt$ denotes velocity. The quantization rule for this system is

$$|p| \, 2L = nh$$

where $|p|$ denotes the constant magnitude of the momentum and n is an integer called the "quantum number". The momentum itself is $+ |p|$ or $- |p|$ according to the direction of motion of the particle. The factor 2 occurs because the length of path of the particle over a complete cycle "there and back" is $2L$. We may thus express the quantization rule in the words "The product of the magnitude of the momentum by the length of path over a cycle is equal to an integral multiple of Planck's constant." The allowed values of the energy E, in this case purely kinetic, are immediately derived from the allowed values of $|p|$.

$$E = \tfrac{1}{2}m\dot{x}^2 = \frac{p^2}{2m} = n^2\,\frac{h^2}{8mL^2}$$

We may now verify that the gaps between successive energy or momentum values of the particle moving freely between two walls are usually negligible. Let us consider the molecules or atoms of helium gas at room temperature. The magnitude of their average kinetic energy of motion in a given direction is about 2×10^{-14} g cm² s⁻². The mass of a helium atom is about 7×10^{-24} g. If then the two walls are 1 mm apart the values of E allowed by the quantization rule are

$$\frac{n^2 \times 6.6 \times 10^{-27} \times 6.6 \times 10^{-27}}{8 \times 7 \times 10^{-24} \times 0.1 \times 0.1}\text{ g cm}^2\text{s}^{-2}$$
$$= n^2 \times 7 \times 10^{-29}\text{ g cm}^2\text{ s}^{-2}$$

Thus the average value of n^2 is about

$$\frac{2 \times 10^{-14}}{7 \times 10^{-29}} \simeq 3 \times 10^{14}$$

and the average value of n is about 1.7×10^7. Hence when n changes to $n + 1$ the energy increases by a fraction $2/n \simeq 1 \times 10^{-7}$. This is so small that we may in this example justifiably ignore the discontinuity in the energy values i.e. ignore quantization. If we had chosen a heavier particle than a helium atom or a larger distance between the walls the effect of quantization would have been still more negligible. At lower temperatures the average energy of a molecule is less but even at a temperature as low as 10°K quantization of the translational motion of molecules is unimportant. We could easily verify that the effect of quantization is quite trivial for the motion of the lightest visible particles and a fortiori for projectiles and planets.

(b) As our second example we take the harmonic oscillator. Since the magnitude of the momentum is not constant the quantization rule cannot be as simple as for the

free particle. By a natural extension of the previous example we might guess that

$$\int p\,\mathrm{d}x = vh$$

where the integration is over a complete cycle "there and back" and v is an integer. We can transform the left side of this equation as follows

$$\int p\,\mathrm{d}x = \int p\dot{x}\,\mathrm{d}t = \int 2T\ \mathrm{d}t = \frac{2\bar{T}}{v}$$

where $\bar{T}$ denotes the average value of T over a complete period of duration $1/v$. But for a harmonic oscillator

$$\bar{T} = \bar{V}$$

where $\bar{V}$ denotes the average value of the potential energy V measured from the equilibrium position as zero. Consequently

$$2\bar{T} = \bar{T} + \bar{V} = E.$$

Our tentative relation may therefore be rewritten as

$$E/v = vh \quad \text{or} \quad E = vhv.$$

We have arrived at this relation by "intelligent guessing" and we have no proof that it is right. According to quantum theory the above formula gives the correct spacing of the energy levels, but the absolute values, when a state of rest at the equilibrium position is taken as zero energy, are

$$E = (v + \tfrac{1}{2})\,hv$$

where v is an integer. The lowest allowed value of the energy lies $\tfrac{1}{2}hv$ above that of the state of rest in the equilibrium position.

(c) As our third example we shall consider a particle free to move in a container. We require three coordinates to describe the position of the particle. We might use cartesian coordinates or spherical polar coordinates, but whatever our choice the required number of coordinates is

three. We describe this situation by the statement that the particle has three "degrees of freedom". According to quantum theory each quantum state is specified by as many quantum numbers as there are degrees of freedom. Let us assume for the sake of simplicity that the container is a rectangular box with edges a, b, c. It is then most convenient to use cartesian coordinates, x, y, z with respect to axes parallel to the edges of the box. With this particular choice of coordinates the problem, in quantum theory as well as in classical theory, can be resolved into three independent sets of relations for the motion in the three directions defined by x, y, z respectively. In mathematical terminology the motion of the particle is "separable" when these coordinates are used. The quantization rules are now

$$|p_x| \times 2a = n_x\, h$$
$$|p_y| \times 2b = n_y\, h$$
$$|p_z| \times 2c = n_z\, h$$

where n_x, n_y, n_z are three independent integral quantum numbers. There are three of them because the particle has three degrees of freedom, and each is of the form already quoted for one-dimensional motion. The energy, being purely kinetic, is given by

$$E = T = \frac{p_x^2 + p_y^2 + p_z^2}{2m} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)$$

If the box is cubic with an edge of length L

$$a = b = c = L$$

and the formula for the energy becomes

$$E = (n_x^2 + n_y^2 + n_z^2)\,\frac{h^2}{8mL^2}$$

All states n_x, n_y, n_z such that $n_x^2 + n_y^2 + n_z^2$ has the same value will have equal energy. For example all the following states have energy $E = 66\ h^2/8mL^2$.

n_x	n_y	n_z	n_x	n_y	n_z
8	1	1	7	4	1
1	8	1	1	7	4
1	1	8	4	1	7
4	5	5	7	1	4
5	4	5	4	7	1
5	5	4	1	4	7

In this case there are 12 distinct quantum states having equal energy and we say that this energy level is "twelve-fold degenerate".

As already mentioned it is sometimes, but by no means always, allowable to ignore the discreteness of quantum states and regard them as forming a continuum. This is allowable when the separation between the energy levels is negligibly small compared with the energy differences or energy changes with which one is concerned. When this condition is satisfied, we say that the system behaves classically. When the condition is satisfied with respect to a particular degree of freedom we say that this degree of freedom behaves classically.

If a certain degree of freedom behaves classically, we may and usually shall treat it classically, i.e. as if the states formed a continuum. Even so it will sometimes be necessary to know how many quantum states are included in an element of the continuum. In the simplest case of a single translational degree of freedom described by the coordinate x and momentum $p_x \equiv m\dot{x}$, the number of quantum states included between x and $x + dx$ and between p_x and $p_x + dp_x$ is $dx dp_x/h$. If we draw a diagram in which the abscissa represents x and the ordinate represents p_x, such a diagram is called a "phase plane". We may then say that there is one quantum state per element of area h in the phase plane.

We may extend this statement to three dimensions. If we imagine x, y, z, p_x, p_y, p_z as a six-dimensional coordinate system this is called phase space for the particle. Then the

number of quantum states is one per element h^3 of six-dimensional phase space.

The statement can be further extended to a system of f degrees of freedom described by coordinates q_1, q_2, ...q_f and momenta p_1, p_2, ...p_f. Then in the 2f-dimensional phase space in which the q's and p's are plotted as coordinates, there will be one quantum state per 2f-dimensional element h^f, provided of course all f degrees of freedom are classical. If they are not classical the statement is still true on the average, but may not be true for an arbitrarily chosen element of phase space.

TEMPERATURE AND PARTITION FUNCTIONS

We shall not attempt to give here a logical definition of temperature. We shall rather state its most important properties.

When two macroscopic systems are placed in contact with each other in such a manner that interchange of energy is possible, then over and above any work that the one system may do on the other, energy will always move from the system at the higher temperature to the system at the lower temperature and this exchange of energy is called a flow of heat. In particular if the two systems have equal temperatures, there will be no flow of heat and they are then said to be in thermal equilibrium. Moreover when heat flows into a system its temperature either increases or remains constant and when heat flows out of a system its temperature either decreases or remains constant. (The case where it remains constant is related to the term "latent heat", but discussion of this is postponed.) Other things being equal (in the interest of simplicity we are deliberately using vague terminology at this stage) increase of temperature involves increase of energy in the system and vice-versa. Consequently, at least in a loose way, temperature is a measure of the energy in a given system.

Energy, like volume, is a typically "extensive property" by which we mean that the energy (or volume) of the whole system is equal to the sum of the energies (or volumes) of the parts of the system. The temperature, like

pressure, on the other hand is a typically "intensive property" by which we mean that in a homogeneous system the temperature (or pressure) of any part is the same as that of the whole. Whereas the energy of the whole system is, as just mentioned, an extensive property, the average energy per molecule in the system is an intensive property. We might then reasonably expect the temperature to be related to the average energy per molecule. We shall see that the temperature in fact determines not only the average energy per molecule, but moreover determines the distribution of the molecules over all possible quantum states.

There is an infinite choice of temperature scales such that everything we have so far said about temperature is valid. There is however one particular kind of temperature scale in terms of which the distribution law over quantum states takes an especially simple form. The temperature on such a scale is called the "absolute temperature" and it is denoted by the symbol T. The distribution law for molecules over quantum states 1, 2, 3, ..., each specified by as many quantum numbers as the molecule has degrees of freedom, may then be expressed as follows. Let N_1, N_2, N_3, ..., denote the number of molecules in the states 1, 2, 3, ..., with energies E_1, E_2, E_3, ..., then

$$N_1 : N_2 : N_3 : ... = e^{-E_1/kT} : e^{-E_2/kT} : e^{-E_3/kT} : ...$$

where k is a constant, called Boltzmann's constant, which is a scaling factor fixing the size of the degree. When the temperature of the triple point of water is defined as 273.16 degrees the scale is called the Kelvin scale and we write for the triple point of water $T = 273.16°K$. On this scale the value of Boltzmann's constant is

$$k = 1.38 \times 10^{-16} \text{ erg deg}^{-1}.$$

The above statement, known as Boltzmann's distribution law, describes by far the most important property of

absolute temperature and it will be our starting point for all problems involving temperature. This statement tells us nothing about how absolute temperature can be measured practically. That is a problem which must be postponed to a later chapter when we shall find it quite easy.

It is sometimes convenient to write Boltzmann's distribution law in the alternative form

$$N_i = \lambda\, e^{-E_i/kT} \qquad \text{(all } i\text{)}$$

where λ has the same value for every quantum state. (Note that we do not call λ a "constant" because that might give the false impression that λ were independent of temperature.) The coefficient λ is called the "activity", or the "absolute activity".

It may happen that we are interested not so much in the number of molecules in a single quantum state i but rather in the number in a certain group of quantum states. In particular we may be interested in the distribution of molecules over the different energy levels, some or all of which may be degenerate. If then we denote by p_r the degeneracy, i.e. the number of independent quantum states, of the energy level E_r and by N_r the number of molecules in this energy level at the temperature T we have

$$\frac{N_r}{p_r e^{-E_r/kT}} = \frac{N_s}{p_s e^{-E_s/kT}} = \frac{N_t}{p_t e^{-E_t/kT}} = \cdots$$

or

$$N_r = \lambda\, p_r e^{-E_r/kT}$$

where the activity λ has the same value for all energy levels.

If we denote by f_i the fraction of molecules in a particular quantum state i, specified by as many quantum numbers as the molecule has degrees of freedom, then we have

$$f_i = \frac{e^{-E_i/kT}}{\sum_j e^{-E_j/kT}}$$

where the summation in the denominator extends over all quantum states. This sum plays an important role in determining the equilibrium properties of molecules. It is sometimes called the "sum of states" (German "Zustandsumme") of the molecule but more usually in English the "partition function" of the molecule. It is denoted by the symbol Q. Thus

$$Q = \Sigma_j e^{-E_j/kT}$$

where Σ_j denotes summation over states, or by

$$Q = \Sigma_r p_r \, e^{-E_r/kT}$$

where Σ_r denotes summation over energy levels.

An important property of a partition function is that it can be factorized whenever the energy is separable with respect to several degrees of freedom. For example if each energy E_i can be expressed as a sum

$$E_i = E'_l + E''_m + E'''_n$$

where the single dash, double dash and triple dash relate to different degrees of freedom or groups of degrees of freedom, each specified by its appropriate quantum numbers, then we have

$$Q = Q' \, Q'' \, Q'''$$

where

$$Q' = \Sigma_l \, e^{-E'_l/kT}$$

$$Q'' = \Sigma_m \, e^{-E''_m/kT}$$

$$Q''' = \Sigma_n \, e^{-E'''_n/kT}$$

We shall call call Q', Q'', Q''' the partition functions for the respective degrees of freedom or groups of degrees of freedom.

SEPARABLE, UNEXCITED AND
CLASSICAL DEGREES OF FREEDOM.
HARMONIC OSCILLATOR

We recall that we describe several degrees of freedom as separable if the energy can be expressed as a sum of independent terms relating to the several degrees of freedom. The partition function then factorizes into factors for the several degrees of freedom. One of the most important cases of separation is between the motion of atomic nuclei on the one hand and of electrons, relative to the nuclei, on the other. This separation is a consequence of the great ratio of nuclear mass to electronic mass. As a consequence of this separation we may in considering the motion of monatomic molecules treat the molecules (atoms) as particles and treat the motion of the electrons in the molecule (atom) as an independent problem.

It may happen that in certain separable degrees of freedom the difference between the energy of the lowest state, called the "ground state", which for convenience we conventionally take as zero, and the energy E_1 of the next state is large compared with kT so that $\exp(-E_1/kT)$ is negligible compared with unity. It follows a fortiori that $\exp(-E/kT)$ is for all the higher states negligible compared with unity. The partition function for this degree of freedom then reduces for all practical purposes to unity and may for many purposes be ignored. Such a degree of freedom is called "unexcited".

Again it may happen that in a group of degrees of freedom separable from all other degrees of freedom, but not necessarily separable among themselves, the energy differ-

ence between the lowest energy level, called the "ground level" and conveniently taken as zero, and the next energy level E_1 is large compared with kT. The partition function

$$Q = p_0 + p_1 e^{-E_1/kT} + \ldots$$

then reduces effectively to p_0 the degree of degeneracy of the ground energy level. Such a group of degrees of freedom is also described as "unexcited".

The energy required to excite an electron in an atom or a molecule is usually comparable with an electron-volt, and the ratio of an electron-volt to Boltzmann's constant is about 1.2×10^4 degrees. Consequently at ordinary temperatures of a few hundred degrees all electronic degrees of freedom may usually be regarded as unexcited. Consequently the electronic partition function of an atom or molecule is usually effectively equal to p_0 the degree of degeneracy of the lowest electronic state. Incidentally for molecules regarded as "saturated" $p_0 = 1$ so that the electronic partition function is effectively unity and may often be ignored. For free atoms p_0 may have other values, for example 2 for alkali metals and 4 for halogen atoms.

The opposite extreme to an unexcited degree of freedom is a "classical" degree of freedom in which the separation between the energies of successive states is small compared with kT. For a classical degree of freedom the precise form of the quantization rule becomes unimportant and in the definition of the partition function the summation over states may be replaced by an integration. The translational motion of an atom in a chosen direction is such a classical degree of freedom. The only quantal information that we need to use for such a degree of freedom is that there is on the average one quantum state per area h in the phase plane. This means that for a particle moving freely between two walls distant L apart the number of states with momentum between p_x and $p_x + dp_x$ is $L dp_x/h$. The energy, entirely kinetic, of such a state is $p_x^2/2m$ where m

denotes the mass of the particle. Consequently the partition function for the translational motion in the direction normal to the walls becomes

$$Q = \int_{-\infty}^{+\infty} \frac{L}{h} \exp\left(-p_x^2/2mkT\right) \, dp_x$$

To evaluate this integral we use the substitution

$$p_x = (2mkT)^{\frac{1}{2}} \xi$$

and so obtain

$$Q = \frac{(2mkT)^{\frac{1}{2}}L}{h} \int_{-\infty}^{+\infty} \exp\left(-\xi^2\right) \, d\xi = \frac{(2\pi mkT)^{\frac{1}{2}}L}{h}$$

Many of the degrees of freedom encountered in practice are either classical, for example the translational motion of molecules, or unexcited, for example the electronic degrees of freedom of molecules. There are however some important degrees of freedom which are neither classical nor unexcited. Most of these are vibrational and can be treated as harmonic oscillations. This is fortunate because the partition function of a harmonic oscillator can be evaluated simply and exactly, as we shall now show.

We recall that the quantum states of a harmonic oscillator of frequency ν have energies given by

$$E_v = (v + \tfrac{1}{2}) h\nu \qquad (v = 0, 1, 2, \ldots)$$

when the energy zero is taken as the state of rest. The partition function is

$$Q = e^{-\frac{1}{2}h\nu/kT} \left(1 + e^{-h\nu/kT} + e^{-2h\nu/kT} + e^{-3h\nu/kT} + \ldots\right)$$

This series is a geometrical progression and can therefore be summed exactly. We obtain

$$Q = e^{-\frac{1}{2}h\nu/kT} \left(1 - e^{-h\nu/kT}\right)^{-1}$$

We note the two limiting cases of an unexcited oscillation

$$h\nu \gg kT \qquad Q \simeq e^{-\frac{1}{2}h\nu/kT}$$

and of a classical oscillation

$$h\nu \ll kT \qquad Q \simeq kT/h\nu$$

IDEAL MONATOMIC GAS

The characteristic property of a gas is that the average separation between a molecule and the nearest other molecule is large compared with the range of interaction between a pair of molecules. Consequently the energy of mutual interaction of the molecules is unimportant compared with the translational kinetic energy of the molecules. For many purposes the energy of interaction may be neglected and when this is done the system considered is called an "ideal gas" or a "perfect gas". No real gas is ideal, but the more dilute it is the more it resembles an ideal gas. In this chapter we shall consider the most important properties of an ideal gas composed of monatomic molecules.

The three translational degrees of freedom of a monatomic molecule are separable from the electronic degrees of freedom. Consequently the partition function Q of a molecule factorizes according to the relation

$$Q = Q_{\text{trans}} Q_{\text{el}}$$

where Q_{trans} relates to the 3 translational degrees of freedom and Q_{el} relates to the electronic degrees of freedom. Moreover, the 3 translational degrees of freedom may be treated as classical and are themselves mutually separable, so that we may write

$$Q_{\text{trans}} = Q_x Q_y Q_z$$

where Q_x, Q_y, Q_z relate to translational motion in the directions of the x, y, z axes respectively.

Let us consider motion in the x direction and assume that the molecule is confined between two walls perpendicular to x and distant L apart. The number of quantum states for motion in the x direction in the element of the phase plane bounded by x, $x + dx$, p_x, $p_x + dp_x$ is $dx dp_x / h$ and the energy of a molecule whose state is represented by this element is

$$E = T = p_x^2 / 2m$$

Consequently the fraction of molecules whose position lies between x and $x + dx$ and whose momentum lies between p_x and $p_x + dp_x$ is

$$\frac{\exp(-p_x^2 / 2mkT) \ dx dp_x / h}{Q_x}$$

where

$$Q_x = \int_0^L dx \int_{-\infty}^{+\infty} dp_x \exp(-p_x^2 / 2mkT) / h$$

We note that the sum by which Q_x is defined has been replaced by a double integral. It follows that the fraction of molecules with momentum between p_x and $p_x + dp_x$, regardless of position, is

$$\frac{\exp(-p_x^2 / 2mkT) \ dp_x}{\int_{-\infty}^{+\infty} dp_x \exp(-p_x^2 / 2mkT)}$$

We notice that the factors h^{-1} have cancelled as in fact they always do for an effectively classical degree of freedom. The integral in the denominator is evaluated by using the substitution

$$p_x = (2mkT)^{\frac{1}{2}} \xi$$

We thus obtain

$$\int_{-\infty}^{+\infty} \mathrm{d}p_x \exp\left(-p_x^2/2mkT\right) = (2mkT)^{\frac{1}{2}} \int_{-\infty}^{+\infty} \mathrm{d}\xi \exp\left(-\xi^2\right)$$
$$= (2\pi mkT)^{\frac{1}{2}}$$

Incidentally this is essentially the same calculation by which in the previous chapter we showed that

$$Q_x = (2\pi mkT/h^2)^{\frac{1}{2}} L$$

We now have for the fraction of molecules with momentum between p_x and $p_x + \mathrm{d}p_x$

$$(2\pi mkT)^{-\frac{1}{2}} \exp\left(-p_x^2/2mkT\right) \mathrm{d}p_x$$

If we express this in terms of velocity u_x instead of momentum $p_x \equiv mu_x$, we have for the fraction $f(u_x)\mathrm{d}u_x$ of molecules with velocity in the x direction between u_x and $u_x + \mathrm{d}u_x$

$$f(u_x)\,\mathrm{d}u_x = (2\pi kT/m)^{-\frac{1}{2}} \exp\left(-mu_x^2/2kT\right)\,\mathrm{d}u_x$$

This is called Maxwell's distribution law after its discoverer. The relation between $f(u_x)$ and u_x is shown in fig. 1.
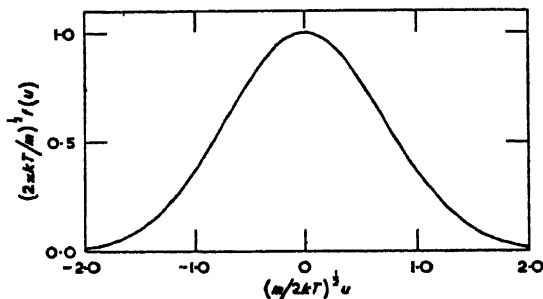

Fig. 1

From Maxwell's distribution law we immediately obtain for the average kinetic energy of motion in the x direction

$$\bar{T}_x = (2\pi kT/m)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} \mathrm{d}u_x \tfrac{1}{2}mu_x^2 \exp\left(-mu_x^2/2kT\right)$$

Using the substitution

$$u_x = (2kT/m)^{\frac{1}{2}} \, \xi$$

we obtain

$$\bar{T}_x = \pi^{-\frac{1}{2}} \, kT \int_{-\infty}^{+\infty} \mathrm{d}\xi \; \xi^2 \exp\left(-\xi^2\right)$$

Integration by parts gives

$$\int_{-\infty}^{+\infty} \mathrm{d}\xi \; \xi^2 \exp\left(-\xi^2\right) = \tfrac{1}{2} \int_{-\infty}^{+\infty} \mathrm{d}\xi \exp\left(-\xi^2\right) = \tfrac{1}{2}\pi^{\frac{1}{2}}$$

so that

$$\bar{T}_x = \tfrac{1}{2}kT$$

The average kinetic energy of motion of a molecule in the x direction is thus $\tfrac{1}{2}kT$. Since the average kinetic energies of motion in the y and z directions obviously have the same values it follows that the total average kinetic energy of a molecule is

$$\bar{T} = \tfrac{3}{2}kT$$

We shall now determine the pressure of a gas of N molecules in a volume V. For the sake of simplicity we shall assume that the gas is contained in a rectangular box, but the answer is not affected by this assumption. The pressure is due to the bombardment of the walls by the molecules and is equal to the transfer of momentum per unit area and per unit time from the molecules to the walls. Consider an element of wall of area A at right angles to the x axis and consider a molecule having velocity u_x in the x direction approaching this wall. The condition that the molecule will reach the wall within the time t is that its distance from the wall should not exceed $u_x t$. Thus the number of molecules with velocity component u_x which hit the element of wall in the time t is equal to the number of molecules with this velocity contained in a volume $Au_x t$. To be more precise, the number of molecules with

velocity component in the x direction between u_x and $u_x + du_x$ hitting the element of area A in time t is equal to

$$\frac{N}{V} A u_x t f(u_x) \, du_x$$

We have ignored the velocity components in the y and z directions because these can only determine where a molecule hits the wall or which molecules hit a particular element of the wall, but can have no effect on the number of molecules hitting a given element. On the assumption that there is perfect reflection at the wall, each molecule on hitting the wall has its momentum in the x direction changed from mu_x to $-mu_x$, so that the momentum transferred to the wall is $2mu_x$. Consequently the momentum transferred to the element of wall in the time t by all molecules with velocity component between u_x and $u_x + du_x$ is

$$\frac{N}{V} A u_x t f(u_x) \, 2mu_x \, du_x = \frac{N}{V} At \, 2m f(u_x) \, u_x^2 \, du_x$$

To obtain the momentum transferred to the element of wall in the time t by all molecules we have to sum over all molecules moving towards the wall, i.e. over all positive values of u_x. We thus obtain

$$\frac{N}{V} At \, 2m \int_0^\infty du_x f(u_x) \, u_x^2 = \frac{N}{V} At \, m \int_{-\infty}^{+\infty} du_x f(u_x) \, u_x^2$$

$$= \frac{N}{V} At \, m \, \overline{u_x^2} = \frac{N}{V} At \, kT$$

Hence the momentum transferred to unit area of wall in unit time is

$$\frac{N}{V} kT$$

and so for the pressure p we have

$$p = \frac{N}{V} kT$$

If we denote the number of moles by n and Avogadro's number by N we have

$$N = Nn$$

so that

$$pV = nNkT$$

or

$$pV = nRT$$

where

$$R = Nk$$

We have thus identified Boltzmann's constant k with the molecular gas constant equal to the molar gas constant R divided by Avogadro's number.

We have also identified the absolute temperature T, first introduced in chapter 2, with the temperature in the equation of state of an ideal gas. Since in fact no gas is altogether ideal the accurate determination of absolute temperature requires a comparison of pV values at several pressures and extrapolation to zero pressure.

Returning now to the energy, which is purely kinetic energy of translation, we see that the energy per mole is $\frac{3}{2}RT$ and its temperature derivative called the molar heat capacity at constant volume is $\frac{3}{2}R$. This value has been confirmed experimentally for the inert elements He, Ne, A, Kr, Xe and the metallic vapours Na, K, Hg.

FREE ENERGY AND TOTAL ENERGY

We obtained the formula for the pressure of a perfect gas composed of monatomic molecules by essentially kinetic considerations. We shall now rederive the formula by a more general and more powerful method making use of the properties of partition functions.

We begin by extending the conception of partition function to a set of several molecules. In the first place we shall consider just a pair of molecules a and b. Then, neglecting any interaction between the two molecules, we have in any state of the pair that its energy is equal to the sum of the energies of the two molecules a and b. Consequently it would seem that the partition function Q of the pair of molecules should be equal to the product of the partition functions Q_a, Q_b of the two molecules. This would in fact be correct if the two molecules were distinguishable. If, on the contrary, the two molecules are identical then we should be wrong in assuming that an interchange of state between the two molecules would change the state of the pair. The correct relation which takes account of the indistinguishability of the two molecules is therefore

$$Q_{\text{pair}} = (Q_{\text{molecule}})^2/2$$

Similarly the correct relation between the partition function of a system of N identical molecules and the partition function of an individual molecule is

$$Q_{\text{system}} = (Q_{\text{molecule}})^N/N!$$

We are now ready to obtain a general relation between the pressure p and the partition function Q of a system containing many molecules. We begin with the elementary formula for the work w done on the system when its volume is increased from V to $V + \mathrm{d}V$

$$w = -p\,\mathrm{d}V$$

We now require a molecular interpretation of w in accordance with quantum theory. For the sake of simplicity we suppose the molecules to be contained in a cubical box of edge L and volume V. Let us begin by imagining that the N molecules were all in the same quantum state specified by the quantum numbers n_x, n_y, n_z. The energy of each molecule would then be

$$E = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8mL^2} = (n_x^2 + n_y^2 + n_z^2)\frac{h^2}{8mV^{\frac{2}{3}}}$$

If all the molecules were in this state and remained in this state, then as the volume changed the energy of the N molecules would change according to the relation

$$N\mathrm{d}E = N\frac{\mathrm{d}E}{\mathrm{d}V}\,\mathrm{d}V$$

and $\mathrm{d}E/\mathrm{d}V$ can be evaluated from the above formula for E. If we further assume that the increase in energy $N\mathrm{d}E$ is equal to the work w done on the system, it follows that

$$p = -N\frac{\mathrm{d}E}{\mathrm{d}V} = -\frac{\mathrm{d}E_{\text{system}}}{\mathrm{d}V}$$

where $E_{\text{system}} = NE$ is the energy of the system of N molecules.

Up to this point we have considered the highly artificial condition that all the molecules are in the same quantum state. We now consider the more realistic condition that the molecular states have their equilibrium distribution corresponding to the temperature T and that as the vol-

ume is changed the distribution is maintained at that corresponding to the temperature T. The number of molecules in the state i of energy E_i is

$$Ne^{-E_i/kT}/\Sigma_i e^{-E_i/kT}$$

Multiplying this by $-dE_i/dV$ and summing we obtain for the pressure

$$p = -\frac{N\Sigma_i \dfrac{dE_i}{dV} e^{-E_i/kT}}{\Sigma_i e^{-E_i/kT}}$$

When we recall the definition of the molecular partition function Q_{molecule}

$$Q_{\text{molecule}} = \Sigma_i e^{-E_i/kT}$$

we see that we have

$$p = NkT\frac{d \ln Q_{\text{molecule}}}{dV}$$

$$p = kT\frac{d \ln Q_{\text{system}}}{dV}$$

We now define a quantity F called the free energy of the system by

$$F = -kT \ln Q_{\text{system}}$$

and can then rewrite the formula for the pressure as

$$p = -\frac{dF}{dV} \qquad \text{(constant } T\text{)}$$

or as

$$dF = -p\,dV \qquad \text{(constant } T\text{)}$$

or as

$$dF = w \qquad \text{(constant } T\text{)}$$

The last formula, which we have derived in the special case of a perfect gas, has in fact a much wider range of validity and may be considered of general application to any system. We see that if a system is kept at a constant

temperature T the work w done on the system is equal
to the increase in its free energy. Thus in a system kept at
a constant temperature the free energy plays a role ana-
logous to that of potential energy in a mechanical, i.e.
temperature-independent system.

We have already obtained an expression for the average
translational energy of a molecule in a system at temper-
ature T. We shall now obtain a more general expression
for the average total energy of a molecule. From the distri-
bution law we obtain for the average energy per molecule $\bar{E}$

$$\bar{E} = \frac{\sum_i E_i\, e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

We can express this in terms of the molecular partition
function Q_{molecule} as

$$E = kT^2 \frac{\mathrm{d}\ln Q_{\text{molecule}}}{\mathrm{d}T}$$

Consequently the total energy U of a system of N mole-
cules at temperature T is

$$U = N\bar{E} = NkT^2 \frac{\mathrm{d}\ln Q_{\text{molecule}}}{\mathrm{d}T} = kT^2 \frac{\mathrm{d}\ln Q_{\text{system}}}{\mathrm{d}T}$$

Dropping the subscript system we have

$$F = -kT \ln Q$$

$$U = kT^2 \frac{\mathrm{d}\ln Q}{\mathrm{d}T}$$

from which it follows that

$$U = -T^2 \frac{\mathrm{d}\,(F/T)}{\mathrm{d}T}$$

or

$$U = F - T\frac{\mathrm{d}F}{\mathrm{d}T}$$

or

$$\frac{U}{T} = \frac{\mathrm{d}\,(F/T)}{\mathrm{d}\,(1/T)}$$

The relation between the total energy U and the free energy F is called the Gibbs-Helmholtz relation. In the particular case that F is independent of T, as in a purely mechanical system, then U is equal to F. In all other cases U is not equal to F. The difference $U-F$ has a simple physical meaning. Consider a fluid system, not necessarily a gas, surrounded by a temperature-bath (thermostat). Suppose that work w is done on the system, e.g. by compressing it. Then $\mathrm{d}F$ is equal to the work w done on the system and $\mathrm{d}U$ is the total energy change of the system. Hence by the principle of conservation of energy $\mathrm{d}(U-F)$ is equal to the energy transferred to the system (from the temperature-bath) so as to maintain its temperature constant. In other words the heat q absorbed from the temperature-bath is $\mathrm{d}(U-F)$.

We recapitulate using Δ to denote the increase of a property in a change at constant temperature T:

$$w = \Delta F$$

$$q = -T \frac{\mathrm{d}\Delta F}{\mathrm{d}T} = -T \Delta \left(\frac{\mathrm{d}F}{\mathrm{d}T} \right)$$

$$w + q = \Delta \left(F - T \frac{\mathrm{d}F}{\mathrm{d}T} \right) = \Delta U$$

These properties of free energy F and total energy U are not confined to fluids but hold generally for any physical system. We shall give two illustrations. As our first example we choose an extensible spring. If l denotes the length of the spring when subjected to a tension X and l^0 the length of the unextended spring, we have according to Hooke's law

$$X = k \frac{l - l^0}{l^0}$$

where k is independent of X but may depend on the temperature. The work required to extend the spring to a length l is by definition

$$w = \int_0^l X \mathrm{d}l = \int_0^l k \frac{(l - l^0)}{l^0} \, \mathrm{d}l$$

Since k may depend on the temperature, the integration can be performed immediately only for constant temperature conditions and the work done on the spring is then equal to the increase in its free energy F. If we conventionally take $F = 0$ for the unstretched spring, we obtain

$$F = w = \tfrac{1}{2}k \, (l - l^0)^2/l^0$$

The corresponding formula for the total energy of extending the spring is

$$U = \tfrac{1}{2} \left(k - T \frac{\mathrm{d}k}{\mathrm{d}T} \right)(l - l^0)^2/l^0$$

and the heat that has to be supplied to the spring to keep its temperature constant during its extension is

$$q = U - F = -\tfrac{1}{2}T \frac{\mathrm{d}k}{\mathrm{d}T}(l - l^0)^2/l^0$$

As our second example we choose a parallel plate condenser. Let A denote the area of each plate, $\pm Q$ the charges on the plates, L their distance apart, and ε the permittivity of the medium between the plates. The potential difference V between the plates (in the rationalized system) is given by

$$V = \frac{QL}{\varepsilon A}$$

The work required to charge the condenser is

$$w = \int_0^Q V \mathrm{d}Q = \int_0^Q \frac{QL}{\varepsilon A} \, \mathrm{d}Q$$

Since ε usually depends on the temperature, the integral can be evaluated immediately only at constant temperature and the work done on the condenser is then equal to the increase in its free energy. If we conventionally take $F = 0$ for the uncharged condenser, we obtain

$$F = w = \frac{Q^2 L}{2\varepsilon A}$$

The corresponding formula for the total energy of charging the condenser is

$$U = \left\{ \frac{1}{\varepsilon} - T \frac{d}{dT} \left(\frac{1}{\varepsilon} \right) \right\} \frac{Q^2 L}{2A}$$

and the heat that has to be supplied to the medium to keep its temperature constant during the charging process is

$$q = U - F = -T \frac{d}{dT} \left(\frac{1}{\varepsilon} \right) \frac{Q^2 L}{2A}$$

Both these examples, and many others, serve to illustrate that, on the whole, the free energy is a simpler quantity than the total energy. This is quite the reverse of the impression conveyed by many elementary physics text-books.

EQUILIBRIUM

In our discussion of isothermal changes of volume we have hitherto tacitly assumed that at every stage the pressure has a well-defined value determined by the volume and the temperature. In other words we have assumed that at every stage of the expansion or compression the system was in hydrostatic equilibrium. Such a change may be called "quasi-static" since at no stage is any large-scale kinetic energy acquired. Such a change is also sometimes called "reversible" because the sequence can be reversed.

A completely different kind of change, to which the above assumptions are altogether inapplicable, is the sudden expansion of a monatomic gas which occurs on the opening of a tap. The gas has well-defined values of V, T, p before and after expansion, but during the expansion while large-scale kinetic energy is developed neither p nor T is well-defined. We shall now investigate the change in the partition function and in the free energy when a tap separating two gases is opened. We shall assume that the whole system is contained in a thermostat so that the initial and final temperature are the same.

We assume that in the initial state there are $N(1-r)$ molecules contained in a volume V' and Nr molecules contained in a volume V''. In the final state the whole volume $V' + V''$ is available to all N molecules. Since the molecular partition function is proportional to the volume

V of the container it will be convenient to write

$$Q_{\text{molecule}} \equiv q\,V$$

where q is independent of V. In the initial state of the system the partition function of the gas confined to the volume V' is

$$\frac{(q\,V')^{N-Nr}}{(N-Nr)!}$$

and that of the gas confined to the volume V'' is

$$\frac{(q\,V'')^{Nr}}{(Nr)!}$$

Consequently the partition function Q_1 of the whole is

$$Q_1 = \frac{(q\,V')^{N-Nr}}{(N-Nr)!} \frac{(q\,V'')^{Nr}}{(Nr)!}$$

Whereas in the initial condition the value of r is prescribed, in the final state all values of r between 0 and 1 are possible. Consequently the partition function Q_2 in the final condition is

$$Q_2 = \sum_{Nr=0}^{Nr=N} \frac{(q\,V')^{N-Nr}}{(N-Nr)!} \frac{(q\,V'')^{Nr}}{(Nr)!}$$

or from the binomial theorem

$$Q_2 = \frac{(q\,V' + q\,V'')^N}{N!}$$

It is physically and mathematically obvious that

$$Q_2 > Q_1$$

This is merely one simple example of a general proposition. When some restraint is removed, e.g. by the opening of a tap, and the system changes to a new state of equilibrium at the same temperature as that of the initial condition, the change is accompanied by an increase in the partition function. Since the free energy F is defined by

$$F = -kT \ln Q$$

the isothermal attainment of equilibrium is accompanied by a decrease of the free energy. We shall now study this decrease quantitatively. We have

$$F_1 - F_2 = kT \ln \frac{Q_2}{Q_1}$$

$$= kT \ln \left\{ \frac{(qV' + qV'')^N}{N!} \frac{(N - Nr)!}{(qV')^{N-Nr}} \frac{(Nr)!}{(qV'')^{Nr}} \right\}$$

$$= kT \ln \frac{(V' + V'')^N}{(V')^{N-Nr}(V'')^{Nr}} - kT \ln \frac{N!}{(N - Nr)!(Nr)!}$$

Since N is a large number we now apply Stirling's approximation

$$\ln N! = N \ln N - N$$

and we obtain

$$\frac{F_1 - F_2}{NkT} = \ln \frac{(V' + V'')}{(V')^{1-r}(V'')^r} - \ln \frac{1}{(1-r)^{1-r}r^r}$$

$$= (1-r) \ln \frac{(1-r)(V' + V'')}{V'} + r \ln \frac{r(V' + V'')}{V''}$$

It can be verified that this expression is never negative and consequently that F_2 is never greater than F_1. So far, so good. But in the particular case of

$$\frac{V'}{V' + V''} = 1 - r \qquad \frac{V''}{V' + V''} = r$$

the expression becomes zero. Hence in this particular case it appears that $F_2 = F_1$, whereas we previously saw that F_2 must always be less than F_1, so that we have an apparent contradiction. This paradox is resolved when a more accurate form of Stirling's approximation is used. It is then found that $(F_1 - F_2)/NkT$ is positive but of the order N^{-1} and so physically negligible.

The physical interpretation of this situation is as follows. In the final state of equilibrium with the tap open all values of r are possible states, but there is an over-

whelming majority of states in which the molecules are distributed almost exactly uniformly between the two volumes. Consequently in the partition function Q regarded as a sum

$$Q = \Sigma_r Q(r)$$

the terms in which r is exactly or almost exactly equal to $r^* \equiv V''/(V' + V'')$ completely swamp all the other terms. As a consequence of this the ratio of Q to $Q(r^*)$ is a number of the order $N^{\frac{1}{2}}$ whereas $Q(r^*)$ itself is of the order N^N. When we take logarithms to obtain the free energy we find that

$$\frac{F \text{ (all possible } r) - F(r = r^*)}{NkT}$$

is of the order $N^{-\frac{1}{2}}$ which is physically entirely negligible.

Since an understanding of this behaviour is specially important, we shall discuss another parallel case namely the attainment of chemical equilibrium between two isomers, e.g. cis and trans dichloro-ethylene. Consider a mixture in which the fraction $1 - r$ is cis and the fraction r is trans. We suppose that initially the conditions are such that transformation of one form to the other is negligibly slow. We next suppose that by the introduction of an active catalyst the transformation of either form to the other is accelerated so that equilibrium is attained. The system is supposed to be contained in a thermostat so that the final temperature is equal to the initial temperature.

We have initially

$$Q_1 = \frac{(Q_{cis})^{N-Nr}}{(N-Nr)!} \frac{(Q_{trans})^{Nr}}{(Nr)!}$$

and finally

$$Q_2 = \sum_{Nr=0}^{Nr=N} \frac{(Q_{cis})^{N-Nr}}{(N-Nr)!} \frac{(Q_{trans})^{Nr}}{(Nr)!}$$

which by use of the binomial theorem reduces to

$$Q_2 = \frac{(Q_{cis} + Q_{trans})^N}{N!}$$

It is mathematically and physically obvious that

$$Q_2 > Q_1$$

and consequently

$$F_2 < F_1$$

The value r^* of r which maximizes Q_1 is given by

$$\frac{r^*}{1 - r^*} = \frac{Q_{trans}}{Q_{cis}}$$

If then r has initially the value r^*, we have by Stirling's approximation

$$\begin{aligned}
\ln Q_1 &= N \ln (Q_{cis} + Q_{trans}) \\
&\quad + (N - Nr^*) \ln (1 - r^*) + Nr^* \ln r^* \\
&\quad - (N - Nr^*) \ln (N - Nr^*) - Nr^* \ln (Nr^*) \\
&\quad + (N - Nr^*) + Nr^* \\
&= \ln \frac{(Q_{cis} + Q_{trans})^N}{N!} \\
&= \ln Q_2
\end{aligned}$$

and consequently to this approximation

$$F_2 = F_1(r^*)$$

Thus the free energy decrease, while always positive, is effectively zero when the initial condition was $r = r^*$. In other words, in the state of chemical equilibrium induced by the catalyst, all values of r are possible, but in fact this equilibrium state differs insignificantly from the state in which r is "frozen" at the value r^*. Thus at equilibrium r has the value which maximizes Q or minimizes F at the given temperature. This statement holds for all kinds of equilibrium, not merely the two examples discussed above.

EQUIPARTITION OF KINETIC ENERGY

In the days before quantum theory there was formulated a principle called the "principle of equipartition of energy". There were various alternative formulations, but whichever of these was chosen the principle was found in some cases to be in agreement with experiment but in others in violent disagreement. The apparent anomaly is, like many other anomalies of classical theory, completely cleared up by quantum theory. The principle is in fact superfluous because it leads only to conclusions which can be derived directly without any use or mention of the principle. Since however the principle is still sometimes quoted, it seems just worth-while discussing its correct formulation and applicability. This is the object of the present chapter, which may however safely be skipped by the reader who is not interested.

In classical degrees of freedom it is allowable to consider the distribution with respect to kinetic energy and with respect to potential energy separately. For the particular case of the translational motion of a particle this is clear from the treatment already given in chapter 4.

The kinetic energy T of the translational motion of a particle of mass m is expressed in cartesian coordinates by

$$T = \tfrac{1}{2}m \left(\dot{x}^2 + \dot{y}^2 + \dot{z}^2 \right)$$

The expression for the same quantity in spherical polar coordinates is

$$T = \tfrac{1}{2}m\,(\dot{r}^2 + r^2\,\dot{\theta}^2 + r^2\sin^2\theta\,\dot{\varphi}^2)$$

In cylindrical coordinates it is

$$T = \tfrac{1}{2}m\,(\dot{r}^2 + r^2\,\dot{\varphi}^2 + \dot{z}^2)$$

We quote these formulae merely to illustrate the fact that, whichever coordinates are used, the kinetic energy is the sum of three terms (because there are three degrees of freedom) each proportional to the square of the time derivative of a coordinate. This can be generalized for more complicated examples of kinetic energy such as the rotational motion of a rigid body. The kinetic energy in f degrees of freedom can be expressed as the sum of f terms each proportional to the square of the time derivative of a coordinate. It follows mathematically from this that for a set of f classical degrees of freedom

$$Q_{\text{kin}} \propto T^{\frac{1}{2}f}$$

where Q_{kin} denotes the factor in Q coming from the kinetic energy. It follows immediately that the average value of the kinetic energy in these degrees of freedom is

$$\overline{E}_{\text{kin}} = kT^2\,\frac{\mathrm{d}\ln Q_{\text{kin}}}{\mathrm{d}T} = \tfrac{1}{2}fkT$$

This formula expresses the principle of equipartition of kinetic energy, which may be stated as follows. The average kinetic energy in each classical degree of freedom is $\tfrac{1}{2}kT$.

There exists no principle of comparable generality relating to potential energy. The average potential energy in a classical degree of freedom depends very much on the nature of the degree of freedom. The only system for which the principle of equipartition contributes anything useful concerning the potential energy is the harmonic oscillator, and of course only when it is effectively classical. In this system, and only this system, the average potential energy (when that of the equilibrium position is taken as zero) is equal to the average kinetic energy and

so equal to $\frac{1}{2}kT$. Consequently the average total energy of a classical harmonic oscillator is kT. This can be verified from the formulae for a harmonic oscillator obtained in chapter 3. When the energy zero is taken as a state of rest at the equilibrium position, the partition function is

$$Q = e^{-\frac{1}{2}h\nu/kT}\left(1 - e^{-h\nu/kT}\right)^{-1}$$

The average energy is therefore

$$\bar{E} = kT^2 \frac{d \ln Q}{dT} = \frac{1}{2}h\nu + \frac{h\nu}{e^{h\nu/kT} - 1}$$

If we denote $h\nu/kT$ by y and expand in powers of y we obtain

$$\bar{E} = h\nu \left\{\frac{1}{2} + y^{-1}\left(1 + \frac{1}{2}y + \frac{1}{6}y^2 + \ldots\right)^{-1}\right\}$$
$$= kT \left(1 + \frac{1}{12}y^2 + \ldots\right)$$

so that

$$E - kT \to 0 \quad \text{as } T \to \infty$$

in agreement with the classical principle of equipartition.

SIMPLE CRYSTAL

We shall consider only the simplest crystals namely those built of single atoms of one element. This class includes the metals. The electronic degrees of freedom may be assumed to be unexcited and will therefore be ignored. There remain the translational degrees of freedom of the atomic nuclei, three for each atom or $3N$ in all for a crystal containing N atoms. The translational motion consists of vibrations of the atoms about their equilibrium positions and the vibrations will usually be of sufficiently small amplitude to be regarded as harmonic. The partition function of the crystal will be of the form

$$Q_{\text{crystal}} = \prod_{i=1}^{i=3N} Q_i$$

where Q_i denotes the partition function of a harmonic oscillator with frequency ν_i. The main problem consists in the determination, by theory or experiment, of the $3N$ natural frequencies of the crystal or, we may say, of the crystal's spectrum. This problem is so complicated as to be practically insoluble unless some approximation is made. Various approximations have been used with various degrees of success. We shall consider in detail only the simplest and earliest of these approximations, that proposed by Einstein. This approximation consists in replacing the product of $3N$ different Q_i's by that of $3N$ equal Q_i's corresponding to a single characteristic frequency ν. With this

approximation we have, taking as energy zero that of the lowest quantum state,

$$Q_{\text{crystal}} = \left(1 - e^{-h\nu/kT}\right)^{-3N}$$

Such an energy zero will, owing to the thermal expansion of the crystal, not be independent of the temperature. It is safer to use an energy zero such as that of the atoms at rest at infinite separation. We then have

$$Q_{\text{crystal}} = e^{N(\chi - \frac{1}{2}h\nu)/kT} \left(1 - e^{-h\nu/kT}\right)^{-3N}$$

where χ denotes the energy required to take an atom from its equilibrium state of rest in the crystal to a state of rest at infinite dispersion.

For the free energy of the crystal we deduce

$$F = -kT \ln Q_{\text{crystal}}$$
$$= -N\chi + \tfrac{3}{2}Nh\nu + 3NkT \ln \left(1 - e^{-h\nu/kT}\right)$$

Both χ and ν must be regarded as dependent on the volume. The pressure is given by

$$p = -\frac{\mathrm{d}F}{\mathrm{d}V} \qquad \text{(const. } T)$$

$$= \frac{\mathrm{d}\chi}{\mathrm{d}v} - \tfrac{3}{2} h \frac{\mathrm{d}\nu}{\mathrm{d}v} - \frac{3h\dfrac{\mathrm{d}\nu}{\mathrm{d}v}}{e^{h\nu/kT} - 1}$$

where $v = V/N$ is the volume per atom. Ordinary pressures, e.g. atmospheric, are from the present point of view negligible so that the above relation does not differ significantly from

$$\frac{\mathrm{d}\chi}{\mathrm{d}v} - \tfrac{3}{2} h \frac{\mathrm{d}\nu}{\mathrm{d}v} - \frac{3h\dfrac{\mathrm{d}\nu}{\mathrm{d}v}}{e^{h\nu/kT} - 1} = 0$$

This relation between $\mathrm{d}\chi/\mathrm{d}v$ and $\mathrm{d}\nu/\mathrm{d}v$ determines the equilibrium value of v the volume per atom at each temperature and so determines the thermal expansion. There is no ground for the statement, sometimes met in text-

books, that thermal expansion is inconsistent with the atomic vibrations being simple harmonic.

For the total energy of the crystal we derive

$$U = F - T\frac{\mathrm{d}F}{\mathrm{d}T}$$

$$= -N\chi + \tfrac{3}{2}Nh\nu + \frac{3Nh\nu}{e^{h\nu/kT} - 1}$$

As the temperature tends to zero

$$U \to -N\chi + \tfrac{3}{2}Nh\nu \qquad (T \to 0)$$

and we recall that this is relative to the infinitely disperse gas as energy zero. If on the other hand we use as energy zero the state with all atoms at rest at their equilibrium positions in the crystal we have

$$U \to \tfrac{3}{2}Nh\nu \qquad (T \to 0)$$

This residual vibrational energy at the absolute zero is called in German "Nullpunktsenergie". The correct literal translation of "Nullpunkt" is absolute zero and so the literal translation of "Nullpunktsenergie" is "absolute-zero energy", which might reasonably be contracted to "zero energy". The current expression "zero-point energy" is an unfortunate mistranslation.

It is usual to introduce Einstein's characteristic temperature Θ_{E} defined by

$$\Theta_{\mathrm{E}} = h\nu/k$$

and U becomes in terms of this

$$U = -N\chi + \tfrac{3}{2}Nk\Theta_{\mathrm{E}} + \frac{3Nk\Theta_{\mathrm{E}}}{e^{\Theta_{\mathrm{E}}/T} - 1}$$

For the heat capacity at constant volume C_v we obtain

$$C_v = \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{3Nk\Theta_{\mathrm{E}}^2/T^2}{(e^{\Theta_{\mathrm{E}}/T} - 1)^2}$$

which can be rewritten in the tidier form

$$C_v = 3Nk \left\{ \frac{\tfrac{1}{2}\Theta_E/T}{\sinh(\tfrac{1}{2}\Theta_E/T)} \right\}^2$$

For one mole (gram atom) of crystal this becomes

$$C_v = 3R \left(\frac{\tfrac{1}{2}y}{\sinh \tfrac{1}{2}y} \right)^2$$

where

$$y = \Theta_E/T = h\nu/kT$$

The function $(\tfrac{1}{2}y/\sinh \tfrac{1}{2}y)^2$ is shown plotted against $1/y$ in fig. 2. We note that for large values of $1/y$, that is at high

—— Einstein's approximation
----- Debye's approximation with $\Theta_D = \tfrac{4}{3}\Theta_E$
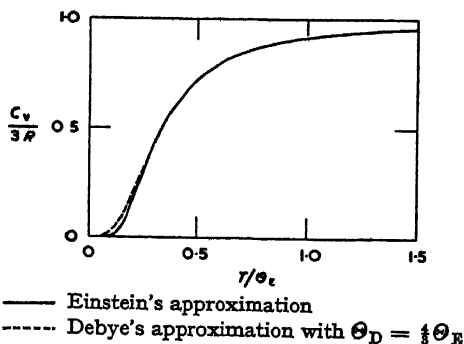
Fig. 2

temperatures, the function approaches unity and C_v approaches the value $3R$. This behaviour corresponds to the empirical law of Dulong and Petit.

At temperatures down to

$$T \simeq \Theta_E/3$$

experimental data on metals can be fitted quite well by Einstein's formula with suitable choice of the parameter Θ_E, but at temperatures much below $\Theta_E/3$ Einstein's formula predicts a much more rapid decrease in C_v than actually occurs. In order to obtain agreement between theory and experiment in this region it is necessary to

make more realistic assumptions concerning the vibration spectrum of the crystal.

The simplest and best known improvement on Einstein's approximation is that of Debye. In this approximation the number of natural frequencies in the range ν to $\nu + d\nu$ is taken to be proportional to ν^2, as in the spectrum of a continuum, up to a maximum frequency ν_{max} so chosen as to give the correct total number of frequencies $3N$. We shall not here give details of this approximation, but only mention a few of its implications. It is usual to introduce a characteristic temperature Θ_D defined by

$$\Theta_D = h\nu_{max}/k$$

When the value of Θ_D is appropriately chosen, the agreement between theory and experiment is just as good as in Einstein's approximation at temperatures down to $T \simeq \Theta_D/4$. The values of Θ_E and Θ_D which fit the same measurements in this range of temperature are inter-related approximately by $\Theta_E = 0.75 \, \Theta_D$. It is evident that Θ_E must be less than Θ_D, since $k\Theta_D/h$ is a maximum frequency whereas $k\Theta_E/h$ is a kind of average frequency over the range between 0 and $k\Theta_D/h$. At temperatures below $T \simeq \Theta_D/4$ Debye's approximation fits much better than Einstein's. In the limit $T \to 0$ Debye's approximation leads to the law $C_\nu \propto T^3$ in satisfactory agreement with experiment at temperatures down to about 1°K. At still lower temperatures there are further complications related to the behaviour of the electrons, which we shall not discuss.

IDEAL DIATOMIC GAS

We turn now to a consideration of an ideal gas composed of diatomic molecules. Apart from the electronic degrees of freedom, which are usually unexcited and which we shall here ignore, there are three degrees of freedom for each atom or six in all. It is most convenient to use the following six coordinates for the molecule: three cartesian coordinates x, y, z for the position of the centre of mass of the molecule; spherical polar coordinates r, θ, φ for the position of one atom relative to the other. The motion of the molecule is then separable and the partition function Q then factorizes as follows

$$Q = Q_{\text{trans}} \, Q_{\text{rot}} \, Q_{\text{vib}}$$

where Q_{trans} relates to the three translational degrees of freedom described by x, y, z; Q_{rot} relates to the two rotational degrees of freedom described by θ, φ; Q_{vib} relates to the mutual motion of atoms along the molecular axis represented by r. We emphasize that there are two rotational degrees of freedom because the orientation of the molecular axis requires two coordinates θ, φ for its description. The statement sometimes met in text-books that the molecule can rotate about two axes is nonsense; the molecule can in fact rotate about any one of an infinite number of axes, but only about one at a time!

The partition function Q_{trans} has exactly the same form as for a monatomic molecule, namely

$$Q_{\text{trans}} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} V$$

where m is the molecular mass and V the volume. The mutual motion of the two atoms along the molecular axis is a vibration about an equilibrium position $r = r_e$ and provided the amplitude is not too great, a condition usually fulfilled, this may be regarded as simple harmonic motion with a frequency ν. Consequently

$$Q_{\text{vib}} = e^{-\frac{1}{2}h\nu} \left(1 - e^{-h\nu/kT}\right)^{-1}$$

It remains for us to say something about Q_{rot}. We shall merely quote the formula for Q_{rot} and shall show that it has the form which might reasonably be expected without giving a formal derivation. Provided the rotational degrees of freedom are classical the formula obtained is

$$Q_{\text{rot}} = 4\pi \left(\frac{2\pi IkT}{h^2}\right)$$

where I denotes the moment of inertia of the molecule, for an unsymmetrical molecule such as CO and

$$Q_{\text{rot}} = \frac{4\pi}{2} \left(\frac{2\pi IkT}{h^2}\right)$$

for a symmetrical molecule such as N_2. When we compare the formula for Q_{rot} with that for Q_{trans} we note the following points

(a) The moment of inertia I in Q_{rot} corresponds to the mass m in Q_{trans}.

(b) The expression in brackets in Q_{rot} is raised to the power 2/2 because the number of rotational degrees of freedom is 2 whereas the number of translational degrees of freedom is 3.

(c) The solid angle 4π in Q_{rot} corresponds to the volume V in Q_{trans}.

(d) The extra factor $\frac{1}{2}$ in Q_{rot} for symmetrical molecules takes account of the fact that when such a molecule

is reversed the final state is not distinguishable from and is consequently the same as the initial state.

Since Q_{trans} has exactly the same form as for a monatomic molecule, while Q_{rot} and Q_{vib} are independent of the volume of the container, the pressure p is given by

$$p = NkT\frac{\mathrm{d}\ln Q}{\mathrm{d}V} = NkT\frac{\mathrm{d}\ln Q_{\text{trans}}}{\mathrm{d}V} = \frac{NkT}{V}$$

just as for a gas of monatomic molecules.

We now pass on to consider the total energy of the gas. We have

$$U = \overline{E_{\text{trans}}} + \overline{E_{\text{rot}}} + \overline{E_{\text{vib}}}$$

where the subscripts attached to E have the same significance as those attached to Q. We shall consider the three terms separately.

For the translational energy we have precisely as for monatomic molecules

$$\overline{E_{\text{trans}}} = NkT^2\frac{\mathrm{d}\ln Q_{\text{trans}}}{\mathrm{d}T} = \tfrac{3}{2}NkT$$

For the rotational energy we obtain similarly

$$\overline{E_{\text{rot}}} = NkT^2\frac{\mathrm{d}\ln Q_{\text{rot}}}{\mathrm{d}T} = NkT$$

in agreement with the equipartition of kinetic energy since there are two rotational degrees of freedom.

Finally for the vibrational energy we obtain

$$\overline{E_{\text{vib}}} = NkT^2\frac{\mathrm{d}\ln Q_{\text{vib}}}{\mathrm{d}T}$$

$$= \tfrac{1}{2}Nh\nu + \frac{Nh\nu}{e^{h\nu/kT} - 1}$$

or

$$\overline{E_{\text{vib}}} = \tfrac{1}{2}Nk\Theta_{\text{v}} + \frac{Nk\Theta_{\text{v}}}{e^{\Theta_{\text{v}}/T} - 1}$$

where Θ_{v} is a characteristic temperature related to the vibration frequency ν by

$$\Theta_{\mathbf{v}} = h\nu/k$$

By addition we obtain

$$U = \tfrac{5}{2} NkT + \tfrac{1}{2} Nk\Theta_{\mathbf{v}} + \frac{Nk\Theta_{\mathbf{v}}}{e^{\Theta_{\mathbf{v}}/T} - 1}$$

We deduce for the heat capacity C_v

$$C_v = \frac{\mathrm{d}U}{\mathrm{d}T} = Nk\left[\tfrac{5}{2} + \left\{ \frac{\tfrac{1}{2}\Theta_{\mathbf{v}}/T}{\sinh\left(\tfrac{1}{2}\Theta_{\mathbf{v}}/T\right)} \right\}^2 \right]$$

For one mole this becomes

$$\frac{C_v}{R} = \tfrac{5}{2} + \left\{ \frac{\tfrac{1}{2}\Theta_{\mathbf{v}}/T}{\sinh\left(\tfrac{1}{2}\Theta_{\mathbf{v}}/T\right)} \right\}^2$$

The function $\{\quad\}^2$ has already been discussed in chapter 8 in connection with crystals. The value of C_v/R tends to $\tfrac{5}{2}$ at low temperatures and to $\tfrac{7}{2}$ at high temperatures.

The value of ν, and so that of $\Theta_{\mathbf{v}}$, for each diatomic molecule is determined from spectroscopic measurements.
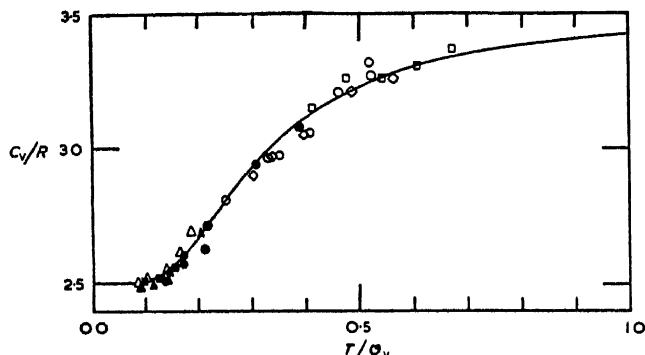

Fig. 3

The formula for C_v can thus be compared with experimental measurements. There is excellent agreement for nitrogen ($\Theta_{\mathbf{v}} = 3350°$), oxygen ($\Theta_{\mathbf{v}} = 2240°$), carbon mon-

oxide ($\Theta_v = 3080°$) and chlorine ($\Theta_v = 796°$) as can be seen from fig. 3.*

As already mentioned we have in our formulae assumed that the rotational degrees of freedom are classical. Whether they are in fact classical depends on the moment of inertia of the molecule. Investigation shows that the rotational degrees of freedom of all diatomic molecules except H_2, HD and D_2 are classical, but that these three molecules owing to their small moments of inertia are exceptions. They in fact have values of C_v/R less than $\frac{5}{2}$ and falling to $\frac{3}{2}$ at low temperatures. This behaviour is entirely in agreement with theory, but we shall not here give details.

* Copied by permission of the Cambridge University Press from "Statistical Thermodynamics" by Fowler and Guggenheim.

PHASE EQUILIBRIUM

The temperature and pressure of a single phase can be varied independently, but when two phases, for example liquid and vapour, of a single substance are present together in mutual equilibrium then the temperature and pressure are not independent. Thus in the case of liquid-vapour equilibrium at each temperature there is a well-defined saturated vapour pressure. At any lower pressure the liquid phase would evaporate and at any higher pressure the vapour phase would condense.

Let us then consider two phases, for example liquid and vapour, of a single substance in equilibrium with each other at a temperature T which determines the pressure p. We suppose the two phase system to be contained in a cylinder closed by a piston subjected to a pressure p, the whole being surrounded by a temperature bath at temperature T. Then by slowly moving the piston out or in the relative amount of the two phases can be varied at constant T, p. We consider a change of volume from V_1 to V_2. We assume that two phases are present throughout; that is to say we must not continue the expansion or compression so far that either phase disappears. We choose as independent variables T, V and regard the free energy F and total energy U as functions of T, V. The pressure p is also a function of T, but is independent of V. We use the subscript 1 to denote the initial state when the volume is V_1 and the subscript 2 to denote the final state 2 when

the volume is V_2. We must emphasize that V_1, V_2 are arbitrarily chosen, but once chosen are constant; they are in no sense temperature-dependent.

In the change from V_1 to V_2 we have

$$F_2 - F_1 = -\int_1^2 p \mathrm{d}V = -p(V_2 - V_1)$$

Since

$$U_1 = F_1 - T\frac{\mathrm{d}F_1}{\mathrm{d}T}$$

$$U_2 = F_2 - T\frac{\mathrm{d}F_2}{\mathrm{d}T}$$

we deduce

$$U_2 - U_1 = -\left(p - T\frac{\mathrm{d}p}{\mathrm{d}T}\right)(V_2 - V_1)$$

which can be rewritten

$$T\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{(U_2 + pV_2) - (U_1 + pV_1)}{V_2 - V_1}$$

$$= \frac{\Delta(U + pV)}{\Delta V}$$

where Δ denotes the increase of a quantity in the change $1 \rightarrow 2$. This important relation is due to Clapeyron.

We note that the numerator $\Delta(U + pV)$ has a simple physical meaning. During the phase change the work w done on the system and the heat q absorbed from the thermostat are determined by

$$w + q = \Delta U$$
$$w = -p\Delta V = -\Delta(pV)$$

and consequently

$$q = \Delta(U + pV)$$

In other words $\Delta(U + pV)$ is the latent heat of the phase change for a quantity of substance such that the expansion is ΔV.

The linear combination $U + PV$ often occurs in formulae relevant to processes taking place at constant pressure. This quantity $U + PV$ is usually denoted by H and has a variety of alternative names of which "heat function" and "enthalpy" are examples. In this notation Clapeyron's formula becomes

$$T \frac{dp}{dT} = \frac{\Delta H}{\Delta V}$$

In the particular case that the first phase is a liquid or solid and the second a vapour it is useful to introduce certain approximations. In the first place we treat the vapour as a perfect gas so that for one mole $V_2 = RT/p$. In the second place we neglect the volume of liquid or solid compared with the volume of the same quantity of gas. If we now let ΔH denote the latent heat of evaporation or sublimation of one mole, we have

$$T \frac{dp}{dT} = \frac{\Delta H}{RT/p}$$

which can be rewritten as

$$d \ln p = - \frac{\Delta H}{R} d \left(\frac{1}{T} \right)$$

If we further regard ΔH as independent of temperature, we can integrate and obtain

$$\ln p = \text{const.} - \frac{\Delta H}{RT}$$

If then $\ln p$ is plotted against $1/T$ we obtain a straight line of slope $-\Delta H/R$.

DIELECTRIC CONSTANT OF A GAS

In this discussion of dielectrics rationalized quantities will be used. Any reader preferring unrationalized quantities need merely replace ε_0 by $\varepsilon_0/4\pi$ and ε_a by $\varepsilon_a/4\pi$ leaving ε unchanged.

We consider a parallel plate condenser. We denote the charge density on the plates by $\pm\,\sigma$, the electric field between the plates by E, and the "polarization", or electric moment per unit volume, in the medium between the plates by P. We further denote the absolute permittivity of the medium by ε_a and the permittivity of empty space by ε_0. We have then according to standard electrostatics

$$\sigma = \varepsilon_a E$$
$$\sigma - P = \varepsilon_0 E$$

so that

$$P = (\varepsilon_a - \varepsilon_0)\,E = (\varepsilon - 1)\,\varepsilon_0 E$$

where ε, defined by $\varepsilon = \varepsilon_a/\varepsilon_0$, is called the relative permittivity or dielectric constant of the medium.

From the physical meaning of P we have

$$P = C\,\bar{\mu}$$

where C denotes the number of molecules per unit volume and $\bar{\mu}$ the average value of the component in the direction of the field of the electric moment of a molecule. This average value $\bar{\mu}$ is the sum of two terms

$$\bar{\mu} = \gamma E + \mu\,\overline{\cos\theta}$$

where γ is the polarizability of the molecule, μ is the absolute value of the permanent electric moment of the molecule and $\overline{\cos\theta}$ is the average value of the cosine of the angle between the permanent electric moment of the molecule and the field.

From the last three formulae we deduce

$$C\left(\gamma E + \mu\,\overline{\cos\theta}\right) = (\varepsilon - 1)\,\varepsilon_0 E$$

or

$$\frac{(\varepsilon - 1)}{C} = \frac{\gamma}{\varepsilon_0} + \frac{\mu\,\overline{\cos\theta}}{\varepsilon_0 E}$$

Our chief interest lies in the determination of $\overline{\cos\theta}$. We consider a molecule whose electric moment makes an angle with the field between θ and $\theta + d\theta$. Such orientations fill a solid angle $2\pi \sin\theta\, d\theta$ and the interaction energy between such a molecule and the field is $-\mu E \cos\theta$. Hence by Boltzmann's distribution law

$$\overline{\cos\theta} = \frac{\displaystyle\int_0^\pi \cos\theta \, \exp\left(\mu E \cos\theta / kT\right)\, 2\pi \sin\theta\, d\theta}{\displaystyle\int_0^\pi \exp\left(\mu E \cos\theta / kT\right)\, 2\pi \sin\theta\, d\theta}$$

We use the substitutions

$$\xi = \mu E \cos\theta / kT \qquad y = \mu E / kT$$

and obtain

$$\overline{\cos\theta} = \frac{1}{y} \frac{\displaystyle\int_{-y}^{y} \xi e^\xi\, d\xi}{\displaystyle\int_{-y}^{y} e^\xi d\xi}$$

The integrals can be evaluated exactly, but since in practice $y \ll 1$ always, it is adequate and more convenient to expand the exponentials and retain only the leading terms. We thus obtain

$$\overline{\cos\theta} = \frac{1}{y}\frac{\displaystyle\int_{-y}^{y}(\xi+\xi^2)\,\mathrm{d}\xi}{\displaystyle\int_{-y}^{y}\mathrm{d}\xi}$$

$$= \frac{1}{y}\frac{\frac{2}{3}y^3}{2y} = \tfrac{1}{3}y = \frac{\mu E}{3kT}$$

We obtain finally

$$\frac{\varepsilon-1}{C} = \frac{\gamma}{\varepsilon_0} + \frac{\mu^2}{3\varepsilon_0 kT}$$

Hence if $(\varepsilon-1)/C$ is plotted against $1/T$ we obtain a straight line of slope $\mu^2/3\varepsilon_0 kT$. An example is shown in fig. 4 which relates to ammonia. Here C_0 denotes the
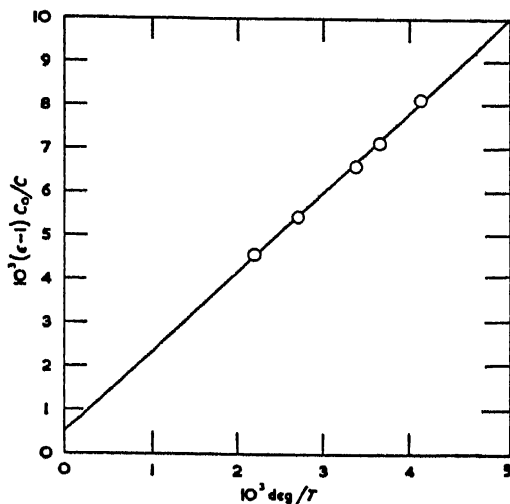

Fig. 4

number of molecules per unit volume at s.t.p. From the straight line we deduce

$$(\varepsilon - 1)\frac{C_0}{C} = 0.5 + \frac{1.84}{T}$$

We have also

$$C_0 = \frac{0.602 \times 10^{24}}{22.4 \times 10^3} \text{ cm}^{-3}$$

$$\varepsilon_0 = 4\pi \text{ esc}^2 \text{ erg}^{-1} \text{ cm}^{-1}$$

(esc here denotes electrostatic unit of charge)

$$k = 1.38 \times 10^{-16} \text{ erg deg}^{-1}$$

From this we obtain

$$\mu^2 = 2.24 \times 10^{-36} \text{ esc}^2 \text{ cm}^2$$

$$\mu = 1.50 \times 10^{-18} \text{ esc cm}$$

The unit 10^{-18} esc cm is called the Debye.

CHEMICAL EQUILIBRIUM

Rather than give a general treatment embracing all types of chemical equilibrium, we shall try to bring out the essential points by the consideration of two simple examples.

As our first example we consider the equilibrium in the gas phase between two isomers such as the cis and trans forms of dichloro-ethylene. This problem has already been briefly mentioned in chapter 6. If we define Q_{cis} as the partition function obtained by summing the Boltzmann factors over all quantum states corresponding to the cis form and define Q_{trans} similarly, then the equilibrium ratio of the numbers of the two isomers is given by

$$\frac{N_{cis}}{N_{trans}} = \frac{Q_{cis}}{Q_{trans}}$$

In using this formula we must take care that we choose the same zero of energy for both kinds of molecules. It is usually more convenient to define each partition function relative to the ground state of the molecule as energy zero. If we do this, we must replace the last formula by

$$\frac{N_{cis}}{N_{trans}} = \frac{Q_{cis}}{Q_{trans}} \exp\left(\frac{E^0_{trans} - E^0_{cis}}{kT}\right)$$

where E^0 denotes the energy of the ground state.

Each of the Q's can be factorized into translational factor and a remaining factor Q_{int} for all the remaining (internal) degrees of freedom including rotations of the

molecule and mutual vibrations of the atoms in the molecule. Since the two isomers necessarily have the same mass, the two translational partition functions are equal and so cancel. Consequently the equilibrium condition reduces to

$$\frac{N_{cis}}{N_{trans}} = \frac{Q_{int, \, cis}}{Q_{int, \, trans}} \exp\left(\frac{E^0_{trans} - E^0_{cis}}{kT}\right)$$

where the right hand side is determined by the temperature and the specific properties of the molecules. It is called the equilibrium constant.

We turn now to our second example, the dissociation equilibrium of iodine

$$I_2 \leftrightharpoons I + I$$
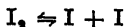
If we use the subscript 1 to relate to monatomic I and the subscript 2 to relate to the molecule I_2, the relations between the number of molecules, the activity and the partition function are

$$N_1 = \lambda_1 Q_1$$
$$N_2 = \lambda_2 Q_2$$

for the two species respectively. It will be shown that the condition for equilibrium between the two species is

$$\lambda_2 = \lambda_1^2$$

which is equivalent to

$$\frac{N_1^2}{N_2} = \frac{Q_1^2}{Q_2}$$

We consider a mixture of N_1 atoms I and N_2 molecules I_2 and initially we consider the values of N_1 and N_2 to be fixed ("frozen"). The partition function of the "frozen" mixture is then

$$Q_{frozen} = \frac{Q_1^{N_1} Q_2^{N_2}}{N_1! N_2!}$$

We now suppose that, for example by the introduction of

a catalyst, the values of N_1 and N_2 become free to change. The partition function of the "thawed mixture" is

$$Q_{\text{thawed}} = \Sigma \frac{Q_1^{N_1} Q_2^{N_2}}{N_1! \, N_2!}$$

where the summation extends over all values of N_1 and N_2 consistent with the conservation of iodine atoms, that is to say subject to the restriction

$$N_1 + 2N_2 = \text{const.}$$

In the thawed condition all sets of values of N_1, N_2 subject to this condition contribute to the sum but there is an overwhelming majority of terms in which N_1, N_2 do not differ significantly from their values in the maximum term. Consequently the equilibrium values of N_1, N_2 are the values N_1^*, N_2^* which maximize the summand. Instead of seeking the maximum term it is more convenient to consider the logarithm of this term. By differentiation we find that it is determined by

$$\ln \frac{Q_1}{N_1^*} \, dN_1 + \ln \frac{Q_2}{N_2^*} \, dN_2 = 0$$

subject to

$$dN_1 + 2dN_2 = 0$$

Eliminating dN_1/dN_2 we obtain

$$2 \ln \frac{Q_1}{N_1^*} - \ln \frac{Q_2}{N_2^*} = 0$$

or dropping the asterisk

$$\frac{N_1^2}{N_2} = \frac{Q_1^2}{Q_2}$$

which is the relation we set out to derive. In using the above formulae we must take care to use a consistent zero of energy. If on the other hand we choose to define Q_1 relative to the ground state of the I atom and Q_2 relative to the ground state of the I_2 molecule, we must use instead the formula

$$\frac{N_1^2}{N_2} = \frac{Q_1^2}{Q_2} \exp(-D/kT)$$

where D denotes the energy required to dissociate an iodine molecule I_2 in its ground state (at rest) into two iodine atoms each in its ground state (at rest).

We now consider the structures of Q_1 and Q_2 in turn. In Q_1 we have a translational factor

$$Q_{1, \text{trans}} = \left(\frac{2\pi m_I kT}{h^2}\right)^{\frac{3}{2}} V$$

and an electronic factor. We recall that electronic degrees of freedom are unexcited so that the electronic partition function reduces to the degree of degeneracy of the ground state. As mentioned in chapter 3 this is unity for saturated molecules, but the I atom is not a saturated molecule and in fact for I

$$Q_{1, \text{el}} = 4$$

For the molecule I_2 we have as described in chapter 9

$$Q_{2, \text{trans}} = \left(\frac{4\pi m_I kT}{h^2}\right)^{\frac{3}{2}} V$$

$$Q_{2, \text{rot}} = \frac{4\pi}{2} \frac{2\pi I kT}{h^2}$$

$$= \frac{4\pi}{2} \frac{\pi m_I d^2 kT}{h^2}$$

where d denotes the distance apart of the two atoms in the I_2 molecule. We also have

$$Q_{2, \text{vib}} = (1 - e^{-\Theta v/T})^{-1}$$
$$Q_{2, \text{el}} = 1$$

Combining all these formulae and using $C = N/V$ to denote molecular concentration, we obtain

$$\frac{C_1^2}{C_2} = \frac{16 \, (2\pi m_I kT/h^2)^3 \, (1 - e^{-\Theta v/T}) e^{-D/kT}}{(4\pi m_I kT/h^2)^{\frac{3}{2}} \, (2\pi^2 m_I d^2 kT/h^2)}$$

$$= \frac{8 \, (m_I kT)^{\frac{1}{2}}}{\pi^{\frac{1}{2}} h d^2} (1 - e^{-\Theta v/T}) e^{-D/kT}$$

Since d, Θ_v and D can be determined spectroscopically, the equilibrium value of $C_1^2/C_2 \equiv K_c$ can be calculated at any given temperature. There is good agreement between the measured and calculated values of K_c over the experimental range of temperatures.

FERMI – DIRAC AND BOSE – EINSTEIN DISTRIBUTIONS

The Boltzmann distribution law which we have been using throughout the previous chapters is in fact only an approximation, but usually a completely adequate one. We shall now say something about the exact distribution laws. There are two such laws. Instead of considering the distribution of molecules over the several states, we shall rather consider the distribution of each quantum state over the possible modes of occupation, i.e. empty or occupied by one molecule or occupied by two molecules or so on. We use the word "molecule" in a general sense to include molecules, atoms, ions, electrons, protons, neutrons and so on.

We first consider the distribution called Fermi-Dirac. It applies to the three fundamental particles: protons, neutrons, electrons. It also applies to any "molecule" composed of an odd number of these particles, e.g. proton, deuterium atom, ^{3}He, ^{13}C, ^{14}N and so on. All such molecules obey the Pauli exclusion principle which states that there must not be more than one molecule in any quantum state. We shall now quote the Fermi-Dirac distribution law. The relative probabilities of a quantum state i of energy E_i being unoccupied or occupied by a molecule are in the ratio $1 : \lambda \exp(-E_i/kT)$ where the activity λ has the same value for all quantum states. This may be expressed in the alternative form: the average number N_i of molecules in the state i is

$$N_i = \frac{\lambda \exp\left(-E_i/kT\right)}{1 + \lambda \exp\left(-E_i/kT\right)}$$

and it is evident that N_i is always less than one.

We turn now to the distribution law called Bose-Einstein. It applies to all "molecules" composed of an even number of fundamental particles, e.g. deuteron, α-particle, H, ^{4}He, ^{12}C, ^{15}N, H_2, D_2 and so on. These are not subject to the Pauli exclusion principle and there is no restriction on the number of molecules in any quantum state. We shall now quote the Bose-Einstein distribution law. The relative probabilities of a quantum state i of energy E_i being occupied by 0, 1, 2, 3, ... molecules are in the ratio

$$1 : \lambda \exp\left(-E_i/kT\right) : \{\lambda \exp\left(-E_i/kT\right)\}^2 : \{\lambda \exp\left(E_i/kT\right)\}^3 \ldots$$

where the activity λ has the same value for all quantum states. This may be expressed in the alternative form: the average number of molecules in the state i is

$$\begin{aligned}
N_i &= \frac{\lambda\exp(-E_i/kT) + 2\{\lambda\exp(-E_i/kT)\}^2 + 3\{\lambda\exp(-E_i/kT)\}^3 + \ldots}{1 + \lambda\exp(-E_i/kT) + \{\lambda\exp(-E_i/kT)\}^2 + \{\lambda\exp(-E_i/kT)\}^3 + \ldots} \\
&= \frac{\lambda\exp(-E_i/kT)\,\{1 - \lambda\exp(-E_i/kT)\}^{-2}}{\{1 - \lambda\exp(-E_i/kT)\}^{-1}} \\
&= \frac{\lambda\exp(-E_i/kT)}{1 - \lambda\exp(-E_i/kT)}
\end{aligned}$$

We can summarize the two distribution laws together as

$$N_i = \frac{\lambda \exp\left(-E_i/kT\right)}{1 \pm \lambda \exp\left(-E_i/kT\right)}$$

where the $+$ relates to the Fermi-Dirac and the $-$ to the Bose-Einstein distribution.

We can now see how these two distribution laws are related to that of Boltzmann. Let the subscript 0 denote the state of lowest energy E_0 and let us consider the situation

$$\lambda \exp\left(-E_0/kT\right) \ll 1$$

so that a fortiori

$$\lambda \exp(-E_i/kT) \ll 1 \qquad \text{(all } i)$$

It then follows that

$$N_i \ll 1 \qquad \text{(all } i)$$

and we may without loss of accuracy replace either formula for N_i by

$$N_i = \lambda \exp(-E_i/kT)$$

which is Boltzmann's distribution law. The physical meaning of the inequalities, which are the conditions for this approximation, is that the number of molecules is small compared with the number of quantum states having energy less than kT.

We state without proof that this condition is satisfied by all the systems, which we have considered, and in fact by almost all systems. The most important exception is the system of conducting electrons in a metal; these obey the Fermi-Dirac distribution law. The Bose-Einstein distribution law is required in the theory of ^{4}He at temperatures comparable with 1°K and the Fermi-Dirac distribution law is likewise required for ^{3}He.

We mention in passing that the Bose-Einstein distribution law also applies to photons (light-quanta). Its application, which we shall not describe, leads to the correct quantitative description of black-body radiation. This phenomenon is of the greatest historical interest since it was the study of this which led Planck to discover the need for quantum theory.